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Gelatin Plasticized with a Biodiesel Coproduct Stream

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Cast gelatin films were plasticized with a biodiesel coproduct stream (BCS). Films were well formed and appeared homogeneous by visual inspection. There is no deterioration in mechanical properties when BCS replaces glycerol as plasticizer. A BCS content of 18–34% resulted in elongations of 35–182%, with corresponding tensile strengths of 45–6 MPa and elastic moduli of 1330–38 MPa. Factor analysis indicated that replacing glycerol with BCS increases elongation but has little effect on tensile strength or modulus. The use of BCS as a plasticizer for biopolymers would increase the value of BCS, increase the value of agricultural fats and oils from which biodiesel is synthesized, and increase the feasibility of fuel production in a biorefinery. The use of low-cost BCS may also increase the feasibility of producing thermoplastics from gelatin and from other biopolymers now more expensive than starch.

Keywords: Gelatin, Glycerol, Biodiesel.

1. INTRODUCTION

Bioproducts, including bioplastics, conserve petroleum and natural gas resources, add little to problems of waste management and, through their composting, contribute to agricultural productivity.[1–3] Bioproduct technologies are needed in which there is a large difference between raw material costs and the value created. One strategy for improving the economics of bioproducts manufacture is to use industrial coproducts, recycled industrial wastes, and abundant agromaterials as feedstocks.

In biodiesel production, the sale of coproduct glycerol has been used to offset the cost of raw materials.[4] However, increased biodiesel production has led to an increase in glycerol supplies, and the resulting lower price of glycerol has caused a decreased cost offset. In fact, the current price of crude glycerol (BCS) is less than five cents per pound, while refined glycerol sells for between 35 cents and 50 cents per pound. Thus, the costs involved in refining the glycerol currently exceed what could be recouped by selling the refined material. As the biodiesel industry continues to expand, these numbers will only worsen as more and more glycerol is generated.

Additional markets for the glycerol coproduct would improve the overall economics of biorefinery operations, and increase the feasibility of fuel production in a biorefinery. If the untreated biodiesel coproduct stream (BCS) could be used without refining, the economics would be further improved.

Glycerol can act as a biopolymer plasticizer by reducing the glass transition temperature, which raises the possibility of marketing biodiesel glycerol for the production of bioplastics. The plasticization of biopolymer thermoplastic films by untreated BCS has not previously been reported.

Gelatin was chosen for the present study because it is already produced in large amounts and is used in a variety of industrial processes.[5] Also, gelatin, unlike some biopolymers, is thermoplastic and can be processed by conventional means, such as extrusion and injection molding.[5,6]

One potential use of gelatin or gelatin waste is in the production of agricultural soil conditioners.[7–11] Polymers that have been examined as soil conditioners include polyacrylamides,[12–14] polyvinyl alcohol[15,16] and polysaccharides,[12] but they have been studied mainly in laboratory simulations; field studies are rare.[17] Gelatin has several properties that make it potentially useful as a soil conditioner material. It is biobased, in contrast to petroleum-based polymers such as polyacrylamides and polyvinyl alcohol; it has a high nitrogen content, in contrast to most polysaccharides; and it is biodegradable.[18]

The purpose of the present study was to compare glycerol and untreated BCS as plasticizers for gelatin. The first objective was to determine whether the presence of the non-glycerol components of BCS would prevent the formation of viable films. The second objective was to compare the mechanical properties of BCS-plasticized films with those of films plasticized with glycerol. The study is,

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therefore, a prerequisite to further consideration of using low-cost BCS to produce thermoplastics from gelatin. The possibility is also recognized of using BCS with other biopolymers now more expensive than starch.

2. EXPERIMENTAL DETAILS

2.1. Materials

Gelatin (Type A G2500) and glycerol were purchased from Sigma Chemicals. The sample of BCS was obtained from OceanAir Environmental Fuel & Glycerine, LLC, Lakeland, FL. It was dark brown in color. Its composition, described in Table I, was assessed as follows. Methanol content was determined by evaporation to constant weight at 22 °C, 15 mm Hg. Glycerol content was determined by enzymatic assay (Glycerol-SL assay, Diagnostic Chemicals Ltd., Prince Edward Island, Canada). Total organics (without glycerol) were determined by washing the BCS in excess hexane; all free fatty acids, esters, and partial glycerides end up in the hexane layer while glycerol remains in the aqueous later. Sodium sulfate was then added to the hexane layer to remove any water present and the hexane was evaporated to dryness. Absolute content of the organic fraction was performed by HPLC.[19]

Methanol was then removed by heating in an open beaker until the temperature reached 72 °C. The weight loss of 17% was assumed to include the 9% methanol and, by difference, an 8% loss of water. The composition of the BCS after methanol removal was therefore taken to be 47% glycerol, 10% other organics, and 43% water; i.e., the organic component consisted of 82% glycerol and 18% other organics.

2.2. Film Casting

Gelatin compositions were formulated as in Table II, which shows the wt percent (%) composition based on a total weight of gelatin and either glycerol or BCS. Previous work,[20,21] had shown that a mid-range composition of gelatin-glycerol cast films, with respect to tensile properties, is approximately 72% gelatin and 28% glycerol. Sample compositions 1–4 represent a control mid-range glycerol film, and films with BCS replacing the glycerol in low-plasticizer, mid-range plasticizer, and high plasticizer compositions.

Table I. Composition of the biodiesel coproduct stream.

Component	Weight percent (%)
Methanol	9
Glycerol	39
Non-glycerol organics, total	8
Free fatty acids	48[a], 53[b]
Alkyl esters	40[b]
Diacylglycerols	5[b]
Monoacylglycerols	1[b]
H_2O	44

[a]Titration. [b]HPLC.

Table II. Composition of gelatin samples showing the weight percent (%) gelatin and either glycerol or BCS.[a]

Sample	Gelatin	Glycerol	BCS
1	72	28	0
2	82	0	18
3	72	0	28
4	66	0	34
5[b]	72	28	0

[a]Combined weight was 20.0 g. Solvent was 400 mL water. Samples 1–4 also contained 30 mL of NH_4OH solution (30%). [b]Identical to sample 1 except sample 5 contained no ammonium hydroxide.

When gelatin films are cast at neutral pH, partial renaturation occurs as the solution is cooled, forming collagen triple-helical structures.[11] Samples 1–4 contained ammonium hydroxide to prevent renaturation. Sample 5 did not contain NH_4OH but was otherwise identical to sample 1; it served as a control to determine the effect of NH_4OH on tensile properties. The presence of ordered structures in sample 5 and the disordered nature of the gelatin chains in samples 1–4 was confirmed by differential scanning calorimetry (DSC) (see below).

The sample components (20.0 g total wt) and 30 mL of NH_4OH solution (30%) were added to 400 mL of water. The samples were heated with stirring in an open beaker to 95 °C. Samples were cast, dried at ambient laboratory temperature and relative humidity, and stored prior to tensile testing for four weeks, also at ambient laboratory conditions.

2.3. Tensile Properties

Before tensile testing, samples were conditioned for two days at a temperature of 23 ± 2 °C and relative humidity of 50 ± 5%, according to ASTM Standard Practice D618. Those conditions were also maintained during the tensile measurements. The standard conditioning environment was provided by an environmentally controlled laboratory room. Tensile measurements were made on an Instron Model 5543 testing system with a 100 N load cell according to ASTM Test Method D882. Specimen width was 1.27 cm; gage length was 5.08 cm; and test speed was 5.08 cm per min.

Samples were then stored in sealed plastic bags for 12 months at ambient laboratory temperature and relative humidity. Following a 48 hr conditioning period under the same conditions used previously the tensile measurements were repeated. The standard conditioning environment was provided by an environmentally controlled laboratory room.

2.4. Differential Scanning Calorimetry

Measurements were made on a Perkin Elmer DSC7 differential scanning calorimeter at a heating rate of 10 °C/min.

2.5. Modeling

Tensile properties were modeled with SAS JMP7 software (SAS Institute, Cary, NC). ANOVA (Analysis of Variance) was first used to identify the factors that contributed to the variation in tensile properties in a statistically significant manner. Those factors were then used to fit the experimental data to a semi-quantitative model. To do so, the Fit Model routine of JMP was used with the standard least squares fitting option and emphasis on effect leverage. Role variables were elongation, modulus, or tensile strength.

For each variable, modeling began using, as effects, the composition factors indicated by the ANOVA analysis as being statistically significant. Cross-terms were added if doing so improved the model statistics. Goodness of fit of the model was measured by R^2, root mean square error, and p value. Low p values reflect the statistical significance of the analysis. For example, a p value of 0.05 indicates that the differences observed in a variable would be expected only once in $1/p = 20$ similar experiments if the compositional factor did not affect the variable. Composition factors with a p value greater than 0.05 were eliminated.

3. RESULTS AND DISCUSSION

Gelatin films, whether plasticized with glycerol or BCS, were well formed and after four weeks appeared homogeneous by visual inspection. After 12 months there was, from visual inspection, evidence of some phase separation in the BCS plasticized films. The tensile properties of gelatin films measured after four weeks and again after 12 months are shown in Table III.

After four weeks, the greatest elongation (182%) was observed in the sample with 34% BCS. The highest modulus and tensile strength values (1.3 GPa and 45 MPa, respectively) were those of sample 2 containing 18% BCS; its elongation was 35%. That material appeared tough and leathery.

Figure 1 shows the dependencies of elongation, modulus, and tensile strength on %BCS for samples 2–4, compared with the glycerol samples 1 and 5. BCS shows typical plasticizing effects; as the amount of BCS increases, the elongation increases, while the tensile strength and modulus decrease. After four weeks, replacing 28% glycerol with 28% BCS appears to have no significant effect on modulus or tensile strength, but increases elongation. After 12 months, the replacement of glycerol with BCS (at 28%) appears to have no significant effect on any of the tensile properties. At 18% BCS aging decreases tensile strength.

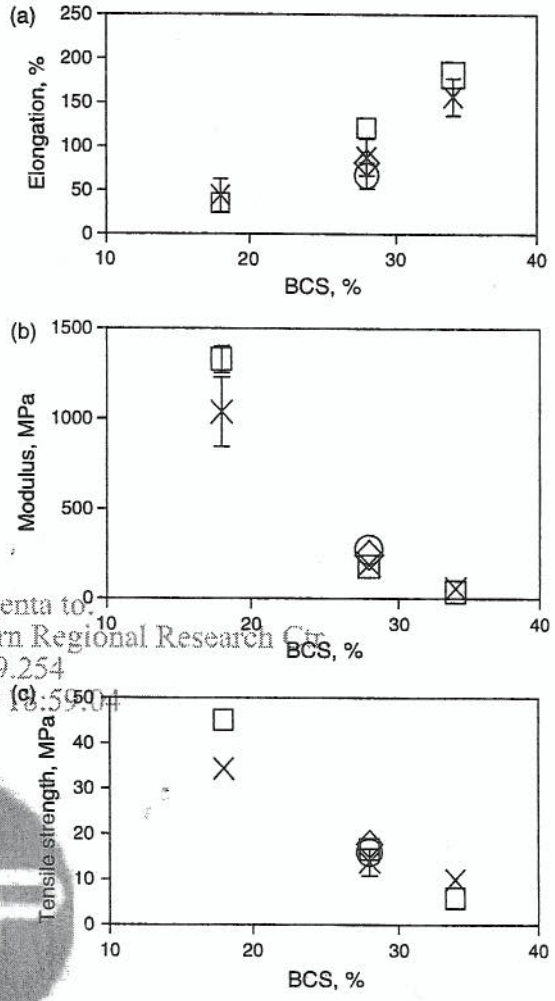

Fig. 1. Dependence of (a) elongation, (b) modulus, and (c) tensile strength of gelatin films on %BCS for samples 2–4, (□ four weeks; X, 12 months), compared with the glycerol control, sample 1, (◇ four weeks; ○ 12 months). Error bars smaller than the symbol size are not shown.

Table III. Elongation at break (ε), Young's modulus (E), and Stress at break (σ) determined by Tensile tests on 4-week-old and 12-month-old gelatin films.[a]

	4 weeks				12 months			
Sample[b]	N	ε (%)	E (MPa)	σ (MPa)	N	ε (%)	E (MPa)	σ (MPa)
1	13	82 ± 7	243 ± 30	17.8 ± 1.6	8	67 ± 15	275 ± 43	15.9 ± 2.5
2	9	35 ± 6	1331± 74	45.1 ± 1.1	8	44 ± 19	1037 ± 193	34.3 ± 1.2
3	10	121 ± 8	179 ± 41	16.6 ± 1.7	9	88 ± 21	189 ± 26	13.8 ± 3.0
4	14	182 ± 12	38 ± 3	5.9 ± 0.5	8	157 ± 21	56 ± 9	9.9 ± 1.5
5	10	43 ± 4	748 ± 51	29.0 ± 1.0	8	49 ± 2	932 ± 43	33.8 ± 0.7

[a]Average values ± standard deviation. N = number of specimens. [b]Average sample thickness ranged from 0.15–0.21 mm.

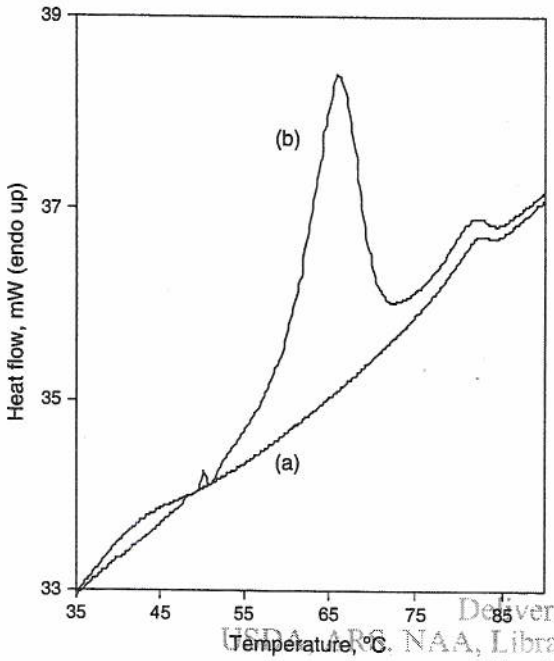

Fig. 2. DSC curves of (a) a gelatin film cast with ammonium hydroxide and (b) a gelatin film cast without ammonium hydroxide.

Figure 2, curve (a), shows the DSC scan of sample 1, containing ammonium hydroxide, and curve (b), shows the DSC averaged over five specimens of sample 5, not containing ammonium hydroxide. When ammonium hydroxide is absent there is evidence of the denaturing of ordered structures characterized by a helix-to-coil transition temperature of 66.0 ± 0.5 °C and ΔH of 24.2 ± 0.6 J/g gelatin. The denaturing feature does not appear when ammonium hydroxide is present. The feature also does not appear during a second scan of samples not containing ammonium hydroxide. Therefore, ammonium hydroxide prevents the partial renaturation of gelatin samples during film formation.

ANOVA indicated those factors that had no significant effect on tensile properties, and were therefore not included in further modeling. For example, aging had no statistically significant effect on any of the tensile properties; p values were 0.7 or larger. Plasticizer type (glycerol versus BCS) had no significant effect on tensile strength or modulus.

The purpose of further modeling, by least-squares fitting, was to obtain semi-quantitative descriptions of the qualitative correlations presented in Table III and Figure 1. The ten average values of Table III were used in the analysis. A summary of the modeling statistics for gelatin films is shown in Table IV. The fits of all three tensile properties were statistically significant; at least 90% of the variance was accounted for (R^2) and all p values were less than 0.05.

The modeling, firstly, confirms the results suggested in Table III and Figure 1 that increasing the amount of plasticizer increases elongation (positive scaled estimate) and decreases modulus and tensile strength (negative scaled estimates). It also confirms that BCS has a larger effect on elongation than pure glycerol (positive scaled estimate for BCS), but replacing glycerol with BCS does not affect modulus or tensile strength. Ammonium hydroxide decreases modulus and tensile strength.

Table IV. Statistical results from modeling properties of gelatin samples.[a]

Property/factor	R^2	rms error	Scaled estimate	p value
Elongation	0.91	18%		0.0002
Plasticizer Amount			64 ± 9	0.0002
BCS[b]			55 ± 10	0.0020
Modulus	0.90	165 MPa		0.0003
Plasticizer Amount			−599 ± 81	0.0002
NH_4OH[c]			−596 ± 130	0.0067
Tensile Strength	0.96	3.0 MPa		0.0001
Plasticizer Amount			−16.4 ± 1.5	<0.0001
NH_4OH[c]			−13.6 ± 2.4	0.0013
Plasticizer Amount × Age[d]			7.6 ± 2.9	0.0411

[a] R^2 is a measure of the variance that is explained by the model: rms is the root mean square error; scaled estimate is a measure of the relative importance of the various factors for a given property. For p value see text.
[b] The scaled estimate is the effect of BCS relative to glycerol.
[c] The scaled estimate is the effect of NH_4OH relative to no NH_4OH.
[d] A cross term indicates that the effect of one factor depends on the other factor.

Secondly, through its scaled estimates, the model gives additional insight by indicating, for example, that the type of plasticizer is approximately equal in importance to the amount of plasticizer in determining elongation. Also, NH_4OH is approximately as important as the amount of plasticizer in reducing modulus and tensile strength. Aging for 12 months has only an indirect effect, on tensile strength, that depends on the amount of plasticizer.

4. CONCLUSIONS

An unmodified biodiesel coproduct stream (BCS) having a ratio of 82 parts glycerol to 18 parts other organic compounds (free fatty acids, alkyl esters, monoacylglycerols, and diacylglycerols) plasticizes gelatin. The non-glycerol components of BCS do not prevent the formation of gelatin films. The range of properties that can be achieved with BCS-plasticized gelatin is broad; BCS contents of 18–34% result in elongations of 35–182%, tensile strengths of 45.1–5.9 MPa, and modulus values of 1331–38 MPa. Tensile properties can be varied by manipulating composition variables. Aging for 12 months decreases tensile strength at low plasticizer level but otherwise has little effect on tensile properties, in spite of evidence of some phase separation. Thus, there is no deterioration in the mechanical properties of cast gelatin films when BCS replaces glycerol as a plasticizer.

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